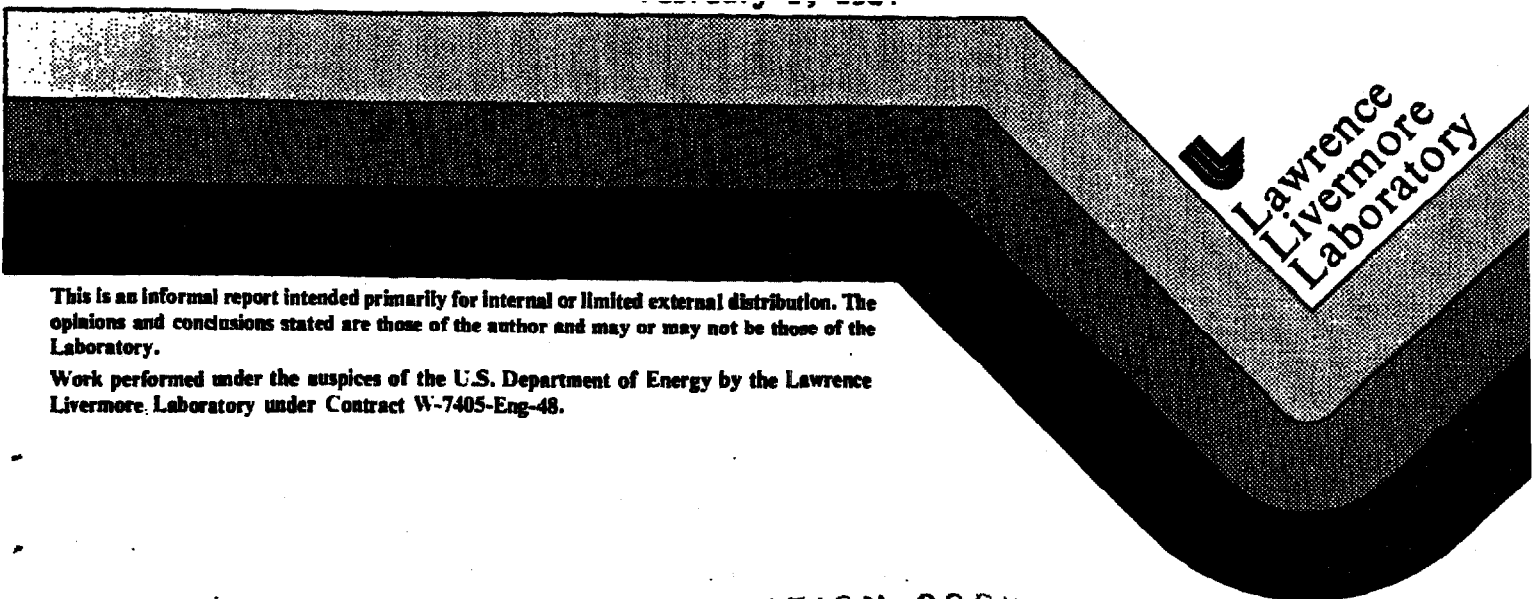


**Plutonium and Americium Behavior in Coral
Atoll Environments**

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February 1, 1984

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PLUTONIUM AND AMERICIUM BEHAVIOR IN CORAL ATOLL ENVIRONMENTS

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ABSTRACT

Inventories of $^{239+240}\text{Pu}$ and ^{241}Am greatly in excess of global fallout levels persist in the benthic environments of Bikini and Enewetak Atolls. Quantities of $^{239+240}\text{Pu}$ and lesser amounts of ^{241}Am are continuously mobilizing from these sedimentary reservoirs. The amount of $^{239+240}\text{Pu}$ mobilized to solution at any time represents 0.08 - 0.09% of the sediment inventories to a depth of 16 cm. The mobilized $^{239+240}\text{Pu}$ has solute-like characteristics and different valence states coexist in solution--the largest fraction of the soluble plutonium is in an oxidized form (+V,VI). The adsorption of plutonium to sediments is not completely reversible because of changes that occur in the relative amounts of the mixed oxidation states in solution with time. Further, any characteristics of $^{239+240}\text{Pu}$ described at one location may not necessarily be relevant in describing its behavior elsewhere following mobilization and migration. The relative amounts of ^{241}Am to $^{239+240}\text{Pu}$ in the sedimentary deposits at Enewetak and Bikini may be altered in future years because of mobilization and radiological decay. Mobilization of $^{239+240}\text{Pu}$ is not a process unique to these atolls, and quantities in solution derived from sedimentary deposits can be found at other global sites. These studies in the equatorial Pacific have significance in assessing the long-term behavior of the transuranics in any marine environment.

1. INTRODUCTION

Many of the questions regarding deep-sea disposal of transuranium elements and other long-lived radionuclides can be partially answered from studies at contaminated, more accessible locations --here some of the processes, reactions, and rates that influence the fate of these radionuclides in the marine environment can be identified and evaluated. Reliable information on the environmental behavior of these radionuclides in the ocean is required to improve our understanding of the pathways that may lead back to man from future practices involving disposal either onto or into marine sediments.

One important question related to the long-term behavior of transuranics in the marine environment is whether the radionuclides, after deposition in the bottom sediments, can return to the water column and eventually reenter biological food chains remote from the point of origin. At some sites contaminated by global fallout or surface discharges where high concentrations are maintained in the overlying water column, mobilization of plutonium from sedimentary sources to solution is difficult to demonstrate (Nelson and Lovett, 1981; Carpenter and Beasley, 1981). However, at sites where plutonium was introduced in sufficient quantities directly onto sedimentary materials or where current inputs to sediments are small, mobilization of plutonium can be easily identified (Noshkin et al., 1978; Noshkin, 1980; Schell et al., 1980; Noshkin and Wong, 1980; Noshkin et al., 1981); Nelson and Metta 1983). For example, the lagoon bottom

sediments at Bikini and Enewetak Atolls, the sites previously known as the Pacific Proving Grounds, were contaminated with fission and activation products from nuclear devices tested there by the United States between 1946 and 1958. Following the last nuclear test at Enewetak in 1958, the residual radionuclides deposited to the lagoon water either settled rapidly to the bottom sediments or remained as dissolved or particulate species in the water and were eventually discharged to open ocean. If we accept the thesis of no mobilization, we would observe a concentration of dissolved plutonium in the lagoon water mass during any time subsequent to 1958 at a level equivalent to that from global fallout in the north equatorial Pacific surface water, the replacement water for the lagoon. Since 1972, a considerable number of filtered lagoon water samples from Enewetak and Bikini have been analyzed and invariably they contained $^{239+240}\text{Pu}$ and ^{238}Pu concentrations in solution and in association with suspended particulates greatly in excess of the fallout background levels in the north equatorial Pacific surface water. The mean concentration estimated for Enewetak and Bikini Lagoons has been relatively constant for at least the last 10 y. It appears that a steady-state condition has been established for $^{239+240}\text{Pu}$ partitioning from the sedimentary reservoirs at the atolls to solution (Noshkin and Wong, 1980).

Plutonium has been emphasized in our previous reports and we have not discussed, in any detail, the relative behavior of americium in these environments. It has been shown that ^{241}Am , resulting from discharges to the northeast Irish Sea, is more effectively associated

with sediment and suspended material than $^{239+240}\text{Pu}$. Results presented herein are addressed to the question of ^{241}Am mobilization at Bikini and Enewetak Atolls and to the geochemical properties of plutonium in regions of the equatorial Pacific marine environment.

2. GENERAL INFORMATION AND EXPERIMENTAL

2.1 General Information

Bikini and Enewetak Atolls, shown with other Marshall Islands Atolls in Fig. 1, were the sites for 22 and 43 nuclear tests, respectively, conducted by the United States between 1946 and 1958. The testing produced close-in fallout debris that was contaminated with transuranic elements and other radionuclides. A large amount of this labelled material entered the aquatic environment of the test sites. Other atolls to the east of the test sites were contaminated to lesser and different degrees by intermediate range fallout.

The United States moratorium on testing began on October 31, 1958 and marked the end of all nuclear testing at Enewetak and Bikini Atolls. The fallout debris and other post-testing activities produced a very heterogenous distribution of radionuclides in the lagoon sediments. Today, quantities of long-lived fission products such as ^{137}Cs , ^{90}Sr , and ^{155}Eu ; activation products such as ^{55}Fe , ^{60}Co , and ^{207}Bi ; and transuranics such as 238 , 239 , 240 , ^{241}Pu and ^{241}Am persist in the atolls' environment. The largest inventory of plutonium at Enewetak and Bikini is associated with lagoon sediments.

Analysis of grab and core samples from the lagoons defined the areal distribution of $^{239+240}\text{Pu}$ and ^{241}Am in the sediment. It is estimated that approximately 250 and 76 Ci, respectively, are associated with the surface 2.5-cm layer at Enewetak, while at Bikini the surface layer inventories of $^{239+240}\text{Pu}$ and ^{241}Am are 310 and 180 Ci, respectively. The inventories to a depth of 16 cm in the sediment column at Enewetak are estimated to be 1200 and 480 Ci of $^{239+240}\text{Pu}$ and ^{241}Am , respectively, and at Bikini the respective values are 1470 and 1140 Ci (Noshkin, 1980).

During the past few years we have been conducting studies at Enewetak and Bikini to better define the physical, chemical, and biological transport mechanisms and fate of the transuranics and other long-lived radionuclides in the aquatic environment. Additional studies have been conducted at other Marshall Islands Atolls and in the equatorial Pacific outside the atolls. These radionuclides are studied mainly to evaluate their impact on critical processes essential for the establishment and continuity of life at the atolls and partly because we recognize these studies can provide significant data for understanding transuranic mobilization and migration processes. The radiological studies at the atolls are therefore germane to problems related to transuranic wastes in the oceans.

2.2 Experimental

2.2.a. Seawater Sample Collections

Large-volume seawater samples obtained for analysis are collected by several methods. Within the lagoon of any atoll, filtered water samples from different depths and locations are collected aboard ship with a pump and hose fitted with an in-line filter. The filter used to remove particulates from the majority of our water samples is a 1- μ m Micro-WyndeII^R, DCCPY filter cartridge (AMF, Cuno Division, Meriden, Connecticut). We have demonstrated that this filter is as efficient in removing suspended particulates from the lagoon water as a 0.2 to 0.3- μ m filter (Noshkin et al., 1974; Wong et al., 1980). Therefore, the soluble concentrations here refer to the quantity passing through a 1- μ m filter, unless otherwise stated. Outside the atolls, water samples are collected at depths using large volume samplers. Plutonium and americium are either preconcentrated from the filtered water in the field by a coprecipitation technique (Wong et al., 1978) and retained on filters or collected in 60-liter sample containers and returned to Lawrence Livermore National Laboratory (LLNL) for processing. When measurements of plutonium oxidation states are made in the field, ²³⁶Pu (VI) and ²⁴²Pu(IV) are used as yield tracers.

2.2.b Analysis

Plutonium is separated from the ashed filters, which contain either particulates or the preconcentrated soluble fraction, by the method described by Wong (1971). The ²⁴¹Am is isolated and purified using a modification of the procedure described by Bojanowski et al.

(1975). Aliquots of ^{242}Pu and ^{243}Am are used as yield tracers except when plutonium oxidation states are determined. Plutonium and americium are finally electroplated onto stainless-steel disks and measured by alpha spectrometry. Some samples from Bikini and Enewetak (sediment, etc.) contain sufficiently high levels of ^{241}Am to be determined directly by gamma spectrometry using Ge(Li) detectors. Duplicates, blanks, and standards are routinely intermingled and processed along with the samples as part of our quality assurance program.

3. RESULTS AND DISCUSSION

3.1 Plutonium Concentrations in Lagoon Seawater

Tables 1 and 2 show the variation of $^{239+240}\text{Pu}$ activity in filtered samples of seawater collected from several locations during different seasons at Enewetak and Bikini. Fallout levels of $^{239+240}\text{Pu}$ in the surface waters of the north equatorial Pacific have averaged 0.4 ± 0.2 fCi/liter over the last 10 y (Noshkin et al., 1981). Of this total concentration, $16 \pm 7\%$ is associated with the particulate filterable material. Concentrations of $^{239+240}\text{Pu}$

Table 1. Concentration of Soluble $^{239+240}\text{Pu}$ (fCi/liter)^a in Seawater Samples Collected at Selected Locations in Enewetak Lagoon During Different Seasons.

1976 ID	10-12/1972 ^b	7-8/1974	5/1976	5-6/1982
5-8-4	13.9	--	22.7	11.8
5-8-2	18	--	31	12.5
5-8-1	32.5	20.7	28.6	20.7
5-7-1	6.8	50	26.3	15.4
5-6-6	44	47	20.8	19.5
5-6-3	15	33	6.9	14.4
5-6-2	7.4	--	1.3	18.3
5-5-4	66	2.1	4.7	38.2
5-5-3	13.1	19	3.5	9.9
5-9-4	--	8.7	15.5	7.2
5-9-3	9.6	--	23.1	13.3
5-9-2	11.6	6.9	7.9	13.7

^aThe 1 σ counting error is less than 10% of listed value.

^bThe 1972 Enewetak water samples were unfiltered. All other concentrations determined in water samples filtered through 1- μm filters.

Table 2. Concentration of Soluble $^{239+240}\text{Pu}$ (fCi/liter)^a in seawater samples collected at selected locations in Bikini Lagoon during different seasons.

1977 ID	12/1972	1-2/1977	9/1982
B-15 Surf	61	27	--
B-15 Btm	58	30	--
B-19	38	32	38
B-20	38	55	31
B-23 Surf	20	44	36
B-23 Btm	8.6	13.3	--
B-25	69	56	--
B-2 Surf	93	74	--
B-2 Btm	79	104	--

^aThe 1 σ counting error is less than 10% of listed value.

greater than fallout background concentrations are found in the water sampled from all locations throughout the lagoons. This is a direct indication that $^{239+240}\text{Pu}$ has been continuously mobilized over the years to solution from the solid phases in these environments.

Ocean water with concentrations of fallout plutonium flows over the eastern and northern reefs and through the southern channels of the atolls. This water mixes with the labelled lagoon water producing complex concentration gradients within the lagoons. Significant differences are noted in the concentration of $^{239+240}\text{Pu}$ with time at some stations in Tables 1 and 2. By comparing the results at any single station, it is not possible with the data available, to discern any consistent trend in the change of concentration with time. Different seasonal and even daily mixing processes influence the concentration at some locations. For example, it has been previously noted that even changes in daily tidal currents effect dissolved plutonium concentrations at specific locations (Noshkin et al., 1974).

One objective, however, was to estimate the fraction of the lagoon inventory transferred to the water column. In order to do so, it was necessary to assume that a reasonable average concentration for the entire lagoon could be determined during periods when sufficient samples were obtained for analysis. Shown in Table 3 are the average soluble and particulate concentrations of $^{239+240}\text{Pu}$ estimated for Enewetak and Bikini Lagoons during the periods indicated. The differences in the average soluble concentration of $^{239+240}\text{Pu}$

Table 3. The $^{239+240}\text{Pu}$ Average Lagoon Water Concentrations ^a.

<u>Enewetak Lagoon</u>				
933 km ² --Lagoon area				
49 m--Average depth				
<u>Month and Year and Number of Water Samples in Parenthesis</u>				
	<u>10-12/72 (35)</u>	<u>7/74 (71)</u>	<u>5/76 (29)</u>	<u>5/82 (23)</u>
Soluble (fCi/liter)	22	25	16	17
Particulate (fCi/liter)	<u>10</u>	<u>19</u>	<u>13</u>	--
TOTAL	32	44	29	
<u>Bikini Lagoon</u>				
629 km ² --Lagoon area				
45 m--Average depth				
<u>Month and Year and Number of Water Samples in Parenthesis</u>				
	<u>12/72 (17)</u>	<u>1-2/77 (26)</u>	<u>9/82 (5)^b</u>	
Soluble (fCi/liter)	42	49	55	
Particulate (fCi/liter)	<u>13</u>	--	--	
TOTAL	55			

^aArithmetic mean values.

^bIncomplete results--value shown represents mean from only 1/5 of total samples obtained.

determined from samples obtained during the periods indicated are not, at this time, considered significant and the assumption is made that the standing average amount of plutonium in the lagoon water mass at any time, is constant. However, future results from the lagoons may show this to be a false premise. Since 1972 the average "soluble" $^{239+240}\text{Pu}$ at Enewetak has been 21 fCi/liter. At Bikini a mean value of 46 fCi/liter is determined from the 1972 and 1977 collections. With the appropriate dimensions for each lagoon, these mean concentrations convert to lagoon standing inventories of 0.96 and 1.3 Ci at Enewetak and Bikini, respectively. Particulate concentrations are not included in these estimates. These quantities represent 0.08 and 0.09%, respectively, of the sediment inventories to a depth of 16 cm. The mean quantity of $^{239+240}\text{Pu}$ mobilized and found in solution at any time represents a small fraction of the inventory associated with the major reservoir of the atolls.

3.2 Other Evidence of $^{239+240}\text{Pu}$ Mobilization in the Central Pacific Atolls

Water and sediment samples have been collected from regions of several northern Marshall Island Atolls east of Enewetak and Bikini (Fig. 1) and from Johnston Atoll, located at $16^{\circ}44'33''\text{ N}$, $169^{\circ}30'59''\text{ W}$, 725 mi W SW of Hawaii. On July 23, 1962, a missile containing plutonium was destroyed while still on the launch pad at Johnston Atoll. The aborted missile dispersed quantities of plutonium

into the surrounding shallow reef environment. A variety of samples have recently been collected from the marine environment of Johnston Atoll to assess the environmental levels of plutonium.

Average concentrations of $^{239+240}\text{Pu}$ in the lagoon water and surface sediments from several of the northern Marshall Atolls are given in Table 4 along with the range in concentrations detected at 13 stations sampled at Johnston Atoll. The data in Table 4 show that filtered lagoon water samples from several of the Marshall Islands contaminated by intermediate range fallout and from Johnston Atoll contain quantities of $^{239+240}\text{Pu}$ in excess of the mean fallout level in the north equatorial surface water outside the lagoons. At Rongelap, the higher concentrations in the lagoon water noted in 1978 were verified in 1981 when a more extensive sampling program was conducted. Mobilization of $^{239+240}\text{Pu}$ from the sediments to the water column is evident at some of these atolls as well.

It has been noted that in shallow basins such as the Great Lakes and the Irish Sea a large fraction of introduced plutonium becomes attached to sedimentary particles and is transferred rapidly to the sediments (Edgington, 1981). One might therefore anticipate observing substantial reductions in the concentration of plutonium in the water of the shallow lagoons of the lesser contaminated atolls such as Ailuk, Likiep, Utirik, or Wotho. The exchange rate of the lagoon water at these atolls is not accurately known but it is estimated to be equal to or greater than 40 d. This period is sufficiently long to permit most of the fallout plutonium entering the lagoon (95%) to be effectively scavenged by the suspended materials during passage

Table 4. The $^{239+240}\text{Pu}$ Mean Water and Sediment Concentrations at Marshall Islands Atolls and Johnston Atoll.

Atoll	Year	Surface (0-3 cm) Collected Sediment (pCi/kg)	fCi/l		
			Soluble	Particulate	Total
Ailuk	1978	8.2	0.57	0.04	0.61
Likiep	1978	7.9	0.58	0.24	0.82
Utirik	1978	16	0.26	0.14	0.40
Wotho	1978	9.5	0.42	0.03	0.45
Rongelap	1978	279	1.31	1.33	2.64
Rongelap	1981	--	7.14	--	--
Rongerik	1978	82	1.20	0.15	1.35
North Equatorial					
Pacific Surface					
Water	1972-1982	--	--	--	0.4 ± 0.2
Johnston	1980	3.5 to 1650	0.4 to 15.5	0.1 to 8.8	--

of water across the shallow reef. However, the mean concentration of $^{239+240}\text{Pu}$ within these lagoons is not distinguishable from the average fallout level in the surface water outside the lagoon. This suggests that an equilibrium has been established at these locations between stabilized forms of fallout $^{239+240}\text{Pu}$ in the surface seawater and the sediments. The same equilibrium is observed at Bikini and Enewetak through the slow, continuous release of plutonium from the sediments to the overlying water column.

3.3 Oxidation States of Mobilized Plutonium in Lagoon Water

Samples of water from Bikini and Enewetak were collected and immediately processed aboard ship to determine the oxidation state(s) of the mobilized plutonium in solution. A selected number of results for both lagoons are shown in Tables 5 and 6, along with several duplicate results. The reproducibility among duplicate analysis is considered satisfactory. The procedure used to separate reduced $^{239+240}\text{Pu}$ (+III, IV) from $^{239+240}\text{Pu}$ (+V, VI) was that described by Lovett and Nelson (1981), modified for our use with water samples larger than 50 l. The modifications are discussed by Wong et al (1983). Both reduced and oxidized forms of $^{239+240}\text{Pu}$ coexist in the lagoon water with oxidized forms generally dominating. On the average, 78% of the total plutonium in solution at both atolls is in the oxidized state.

It is difficult to identify any clear regularities or trends in the results, but, in some cases, samples from stations near the reef and near the sediment-water interface contain relatively larger

Table 5. The $^{239+240}\text{Pu}$ Oxidation States in Filtered Seawater at Lagoon Stations at Bikini Atoll.

Station Number	Date	Depth	Reduced	Oxidized	Total	Percent Oxidized
			(+III, IV) (fCi/liter)	(+V, VI) (fCi/liter)		
B-1	2/81	Surf	8.9 ± 0.4	11.7 ± 0.5	20.6 ± 0.8	57 ± 3
B-1	2/81	10 m	13.3 ± 0.5	12.0 ± 0.8	25.3 ± 1.6	46 ± 4
B-J	2/81	25 m	13.2 ± 0.5	16.1 ± 1.6	29.3 ± 3.2	55 ± 7
B-5 Reef	2/81	Surf	26.5 ± 2.1	66.3 ± 6.3	92.8 ± 8.4	71 ± 10
B-6 Reef	2/81	Surf	5.7 ± 0.3	31.2 ± 1.2	36.9 ± 1.8	85 ± 6
B-20 Reef	2/81	Surf	3.7 ± 0.4	19.5 ± 2.0	23.2 ± 2.6	84 ± 12
B-1 Reef	2/81	Surf	5.7 ± 0.3	6.1 ± 0.5	11.8 ± 0.8	52 ± 4
B-19	9/82	Surf	6.0 ± 1.2	31.8 ± 2.2	37.8 ± 3.4	84 ± 4
B-18	9/82	Surf	<0.5	53.5 ± 3.7	5.4 ± 3.7	99 ± 7
B-18	9/82	29 m	41.0 ± 2.5	78.2 ± 3.1	119 ± 6	66 ± 4
B-26	9/82	Surf	<0.5	48.4 ± 1.9	48.9 ± 1.9	99 ± 3
B-26	9/82	48 m	4.1 ± 0.5	14.3 ± 1.0	17.4 ± 1.6	80 ± 9

Table 6. The $^{239+240}\text{Pu}$ Oxidation States in Filtered Seawater at Lagoon Stations at Enewetak Atoll (fCi/liter).

Station			Reduced	Oxidized		
Number	Date	Depth	(+III, IV)	(+V, VI)	Total	Percent Oxidized
E-24	10/79	surf	4.7 ± 0.9	10.4 ± 0.8	15.1 ± 1.7	69 ± 9
E-24	10/79	Duplicate	4.6 ± 1.1	13.0 ± 1.6	17.6 ± 2.6	74 ± 14
E-24	10/79	10m	7.5 ± 1.1	23.0 ± 1.4	30.5 ± 2.4	75 ± 8
E-24	10/79	25 m	8.1 ± 1.3	27.4 ± 2.7	35.5 ± 3.6	77 ± 11
E-10	10/79	Surf	0.9 ± 0.3	8.7 ± 1.7	9.6 ± 2.0	91 ± 26
E-10	10/79	Duplicate	1.1 ± 0.4	6.4 ± 0.8	7.5 ± 1.1	85 ± 16
5-6-1	10/79	Surf	5.2 ± 0.4	20.0 ± 1.4	25.2 ± 1.8	79 ± 8
E-10	6/82	Surf	1.3 ± 0.1	5.3 ± 0.3	6.6 ± 0.3	80 ± 6
6-2-1	6/82	Surf	12.3 ± 0.7	26.9 ± 1.3	39.2 ± 2.3	69 ± 5
6-2-1	6/82	Replicate	12.3 ± 1.1	25.2 ± 1.8	37.5 ± 2.1	67 ± 6
6/82	Replicate		--	--	38.2 ± 1.1	--
6-2-5	6/82	Surf	2.9 ± 0.3	13.0 ± 0.9	15.9 ± 1.3	82 ± 9
6-2-5	6/82	Duplicate	--	--	14.8 ± 0.4	--
6-2-5	6/82	22 m	2.7 ± 0.2	10.9 ± 0.8	13.6 ± 1.1	80 ± 8
6-2-5	6/82	Duplicate	--	--	12.8 ± 0.4	--
6-1-3	6/82	Surf	2.5 ± 0.3	11.9 ± 0.7	14.4 ± 1.0	83 ± 8
6-1-3	6/82	Duplicate	--	--	13.7 ± 0.4	--
5-31-7	6/82	Surf	1.8 ± 0.4	10.3 ± 0.7	12.1 ± 1.0	85 ± 7
5-31-7	6/82	Replicate	1.7 ± 0.2	8.7 ± 0.6	10.4 ± 0.8	84 ± 7
5-31-7	6/82	Replicate	--	--	10.5 ± 0.4	--

fractions of reduced plutonium in solution than found in mid-lagoon surface samples. Over 90% of the $^{239+240}\text{Pu}$ found associated with sedimentary or particulate material in the lagoon is in the reduced state (see footnote Table 7). Therefore, near-bottom or reef water would be expected to contain relatively higher concentrations of recently exchanged, reduced plutonium. After desorption of reduced and oxidized species, the +III, IV state disappears from solution either by oxidation to the higher state or loss by adsorption onto newly exposed surfaces. Laboratory experiments discussed in the next section provide results that support the former possibility. In either case, the oxidized forms of plutonium become the dominate species in water with longer residence times in the lagoons (stations B-18, B-26, and E-10) and probably persist as a complexed, unreactive species. However, since the reduced forms of plutonium are ubiquitous in all but a few samples, it is possible that the reduced plutonium may also be stabilized by complexation to some degree, but the stability of the complex may change with time.

3.4 Exchange of Plutonium Between Sediments and Seawater

At any location within Enewetak and Bikini Lagoons, bottom sediments may be found consisting of different quantities of fine- and coarse-grained carbonate material, shells, forams, coral fragments, and Halimeda debris. All these components have different surface areas and therefore different sorptive characteristics. Transuranics are associated with all components of the benthic environment (Noshkin,

1980), and their rate of desorption to solution may relate to the composition of the sediment.

To mimic the exchange characteristics of $^{239+240}\text{Pu}$ from the sediments to solution observed in the environment, we conducted experiments in the laboratory (or aboard ship) with different, freshly collected sediments to arrive at a value for the distribution coefficient K_d for plutonium. We placed quantities of different sedimentary materials in plastic containers and added volumes of filtered, equatorial Pacific surface seawater with very low concentrations of dissolved plutonium (0.4 fCi/liter). The containers were shaken for various periods to mix the contents. Then, the water was separated from the sediments by filtration through 0.2- μm filters. Tracers were added to the solution phase and plutonium was separated and analyzed by the procedures described. Sediments were dried, dissolved, and analyzed for plutonium. The range in the apparent K_d values (total $^{239+240}\text{Pu}$ on sediments in pCi/kg divided by total $^{239+240}\text{Pu}$ in solution in pCi/liter) based on the analyses of 18 different lagoon sediments was between 0.5 and 5.2×10^5 with an average K_d for $^{239+240}\text{Pu}$ of 2.3×10^5 (Noshkin and Wong, 1980).

With the sediment inventory values and the K_d for plutonium of 2.3×10^5 , one can construct a simple model to predict average concentrations expected in the lagoon water by assuming that the plutonium in solution at any time is in equilibrium with that in the sediments. At any time the amount of plutonium in solution is limited by the saturation of the solution under equilibrium conditions. The rate at which water and its dissolved plutonium is flushed from the

lagoon is balanced by input of the lesser-contaminated ocean water that is rapidly equilibrated with remobilized plutonium from the sediments. Assuming that this steady-state condition can be achieved, the mean plutonium inventory and concentrations in lagoon water, computed from a K_d of 2.3×10^5 as defined above, is 0.99 Ci (23 fCi/liter) at Enewetak and 1.3 Ci (41 fCi/liter) at Bikini. There is good agreement between the average quantities of $^{239+240}\text{Pu}$ predicted and the average values shown in Table 3. The agreement between the calculated and the measured average concentrations, where one would accept a factor of 5 as being good agreement because of the range of K_d values determined, supports the contention of a steady-state condition and demonstrates the general usefulness of this simple model in predicting long-term average concentrations in the lagoon water.

Additional time-dependent experiments and oxidation state determinations were conducted in the laboratory with contaminated lagoon sediments. Results for the different oxidation states released to seawater from fine and coarse sediments obtained from two different locations in Enewetak Lagoon are shown in Tables 7 and 8. Of the total $^{239+240}\text{Pu}$ associated with the sediments used to generate these results, $96 \pm 2\%$ was in the reduced state. When fresh seawater initially contacts the fine and coarse sediment fractions shown in Table 7, there is a rapid release of both oxidized and reduced forms of $^{239+240}\text{Pu}$ into solution. As the contact time with the sediment increases, the K_d for reduced plutonium increases, indicating a disappearance of the reduced forms from solution. Concurrently, the K_d determined for the oxidized forms of plutonium decreases slightly, showing that the oxidized forms of $^{239+240}\text{Pu}$ in solution

Table 7. The $^{239+240}\text{Pu}$ Oxidation States Released to Seawater and K_d Values After Mixing with Lagoon Sediments from Enewetak Off E-2 (NW Lagoon).

Sample ID	Mixing Time (h)	Sediment ^a Concentration (pCi/g)	Reduced (III,IV) (fCi/liter)	Oxidized (V, VI) (fCi/liter)	$K_d \times 10^{5b}$		
					Apparent	Reduced	Oxidized

<u>Fine Fraction (<0.5 mm)</u>							
439/440	3.5	20.1 (2) ^c	51 (14)	66 (12)	1.7	3.4	0.12
443/444	3.5	17.5 (2)	71 (13)	48 (17)	1.5	2.4	0.15
399/400	24	17.1 (2)	23 (22)	54 (9)	2.2	7.1	0.13
411/412	24	19.0 (2)	14 (41)	67 (14)	2.3	13.0	0.11
427/426	74	19.5 (2)	12 (23)	80 (8)	2.1	15.6	0.10
<u>Coarse Fraction (>5 mm)</u>							
379/380	26	2.49 (4)	7 (54)	13 (26)	1.2	3.4	0.08
383/384	26	2.89 (5)	3.5 (38)	28 (13)	0.9	7.9	0.04
391/392	81	2.93 (3)	<0.3	32 (11)	0.9	>10	0.04

^a $96 \pm 2\%$ of total $^{239+240}\text{Pu}$ associated with sediments in reduced state

3.3-9.2 g of sediment mixed with 0.95 liter of filtered seawater.

^b Apparent K_d = total concentration of $^{239+240}\text{Pu}$ in dry sediment (pCi/kg)/total concentration of $^{239+240}\text{Pu}$ in solution (pCi/liter). Reduced K_d = 0.96 total concentration in dry sediment/reduced concentration in solution. Oxidized K_d = .04 total concentration in dry sediment/oxidized concentration in solution.

^c Values in parentheses are the 1σ counting error expressed as percent of the value listed.

Table 8. The $^{239+240}\text{Pu}$ Oxidation States Released to Seawater and K_d Values After Periods of Mixing with Lagoon Sediments from Enewetak off E-24 (E Lagoon).

	Mixing	Sediment	Reduced	Oxidized			
Sample	Time	Concentration	(III, IV)	(V, VI)	$K_d \times 10^5$		
ID	(h)	(pCi/g)	(fCi/liter)	(fCi/liter)	Apparent	Reduced	Oxidized
<hr/>							
<u>Fine Fraction (<0.5 mm)</u>							
359/360	24	14.3 (3)	23 (22)	222 (6)	0.6	6.0	0.03
363/364	24	14.6 (2)	56 (19)	181 (7)	0.6	2.5	0.03
367/364	94	17.0 (3)	40 (14)	244 (8)	0.6	4.1	0.03
371/372	94	16.9 (3)	53 (15)	238 (7)	0.6	3.1	0.03
377/620	2880	17.7 (3)	58 (15)	220 (6)	0.6	2.6	0.03
<u>Coarse Fraction (>0.5 mm)</u>							
339/340	23	6.03 (5)	15 (19)	42 (10)	1.1	3.9	0.06
343/344	23	5.85 (5)	15 (21)	47 (13)	0.9	3.7	0.05

NOTE: See footnotes, Table 7.

increase over the same period. This increase of oxidized forms of plutonium can be accounted for by assuming that the reduced forms initially mobilized are slowly oxidized in solution. These results constitute confirmation of the field observations where both oxidized and reduced species are initially mobilized to lagoon bottom water. The concentration of reduced plutonium decreases with time as a result of redox reactions, leaving the oxidized forms of plutonium as the dominate dissolved species in solution.

Results in Table 8 also show, rapid mobilization of both forms to solution followed, however, by no apparent change in concentration of either species as the contact time with the E-24 sediments increases. At 94 h, the K_d values for both reduced and oxidized forms of $^{239+240}\text{Pu}$ from the fine sediment experiment are less than the values at 74 h of contact with sediments from E-2 shown in Table 7. The reasons for the different behavior of the E-2 and E-24 sediments is unknown and we can only speculate that both mobilized species are stabilized in solution possibly by complexing agents derived from materials present in the sediments at E-24 but absent at E-2. For whatever the reasons the reduced forms of $^{239+240}\text{Pu}$ mobilized to solution from the region of station E-24 are capable of remaining in a dissolved state for longer periods of time as suggested by the field measurements. Plutonium mobilized to solution from any region of either lagoon could be expected to behave between the examples shown in Tables 7 and 8.

Once the reduced plutonium is oxidized in solution, the process of readsorption of $^{239+240}\text{Pu}$ onto sediment appears to be determined by an accumulation factor different than the value obtained from the

desorption experiments. In Table 9, two examples are shown where contaminated water from Enewetak Lagoon is equilibrated with quantities of relatively uncontaminated sediment from Kwajalein Atoll. The oxidation states of plutonium associated with these sediments were not determined. The first example shows the initial and final $^{239+240}\text{Pu}$ concentrations in seawater from the region of E-24 after mixing with sediments for 22 h. Within experimental error, there was no difference noted between the initial and final concentrations of either reduced or oxidized forms of plutonium in solution. The computed apparent K_d , determined by comparing the final total water and sediment concentrations, is significantly less than the desorption values in Tables 7 and 8 determined after 24 h of mixing contaminated sediment with uncontaminated water.

The second set of results were generated using seawater aliquots in contact with sediments for longer periods of time. Unfortunately, the water selected was not as highly labelled with $^{239+240}\text{Pu}$ as had been anticipated, and therefore the errors associated with the determinations are large. The results do show a complete disappearance of reduced $^{239+240}\text{Pu}$ from solution after 72 h, but it is impossible to assess if this loss resulted from the operation of the redox equilibrium or sorption onto the sediment. There was a definite loss by resorption of the oxidized state of $^{239+240}\text{Pu}$ onto the sediment. The sediment concentrations increased from 8 ± 3 fCi/g to 15 to 18 fCi/g after equilibration. Each of the sediment samples contacted with the water for 24, 72, and 3×10^3 h gained, on the average, 29 ± 9 fCi while 33 ± 8 fCi, on the

Table 9. Equilibration of $^{239+240}\text{Pu}$ -Labelled Seawater with Lesser-Contaminated Sediments.

Contact time (h)	Sediment Concentration (fCi/g)	Reduced (fCi/liter)	Oxidized (fCi/liter)	Total	Apparent $K_d \times 10^3$
0		3.7 (11) ^a	19.5 (10)	23.2 (11)	--
22	4.7 (21)	5.5 (8)	20.2 (5)	25.7 (6)	0.2
0	-- ^b	1.2 (54)	8.7 (19)	9.7 (18)	--
24	18(12)	1.2 (75)	5.2 (27)	6.4 (26)	2.8
72	15(15)	0.7 (40)	3.4 (14)	4.1 (13)	3.7
3×10^3	17(15)	<0.2	4.3 (19)	4.4 (19)	3.9

^aValues in parentheses are the 1σ counting error expressed percent of the value listed.

^bInitial sediment concentration--8 (37) fCi/g; 3.84, 2.90 and 3.3 g of sediment used in the respective equilibration experiments.

average, was lost from solution. The plutonium lost from solution can be accounted for by the gain on the sediments. The apparent K_d computed in Table 9 is the value for total plutonium in solution to total plutonium in the sediments. The resorption in each timed experiment was rapid in as much as there was no further change in the concentration of oxidized forms of plutonium remaining in solution after 24 h of equilibration.

While it appears possible to predict the desorption of $^{239+240}\text{Pu}$ using a K_d of approximately 2.3×10^5 , the readsorption process of mobilized plutonium results in lower accumulation factors and is more complex than predicted by the simple partitioning between solution and solid phases because of the different chemistries of mixed oxidation states in solution.

3.5 Relationships Between ^{241}Am and $^{239+240}\text{Pu}$

Concentration profiles to a depth of 1000 m in the equatorial Pacific west of Bikini (Station WBO) indicate that ^{241}Am in the ocean is more strongly associated with particles than $^{239+240}\text{Pu}$ (Table 10). Some data from the water column near Johnston Atoll (Station JAO) are provided in Table 11 to highlight certain features of the results at WBO. The presence of plutonium concentrations, that are orders of magnitude higher in the surface waters at WBO compared to the fallout levels in the surface layers at JAO show that mobilized forms of $^{239+240}\text{Pu}$ are passed from the lagoon to the water mass of the north equatorial Pacific. The concentrations throughout the

Table 10. Transuranics in the Water Column to 1000m at Station WBO 11°35'N
165°05'E - September 1980.

Depth (m)	<u>$^{239+240}\text{Pu}^a$ (fCi/liter)</u>		<u>^{241}Am (fCi/liter)</u>		<u>$^{241}\text{Am} : ^{239+240}\text{Pu}$</u>	
	Prefilter	Solution	Prefilter	Solution	Prefilter	Solution
Surf	lost	4.6 (4)	lost	lost	--	--
100	0.04 (22)	0.51 (11)	lost	0.17 (45)	--	0.33 (46)
200	0.20 (15)	0.76 (12)	lost	0.22 (26)	--	0.29 (29)
300	0.46 (11)	0.89 (15)	0.54 (47)	0.19 (50)	1.2 (48)	0.21 (52)
400	0.49 (11)	1.5 (9)	0.61 (23)	<0.03	1.2 (25)	<0.02
500	0.21 (25)	1.9 (7)	0.79 (20)	0.11 (40)	3.8 (32)	0.06 (40)
600	0.03 (60)	1.6 (7)	0.38 (28)	0.18 (50)	12 (65)	0.11 (50)
700	0.12 (30)	1.6 (7)	0.77 (16)	0.52 (37)	6.4 (34)	0.32 (38)
800	0.12 (36)	2.2 (6)	0.65 (25)	0.35 (35)	5.4 (44)	0.16 (36)
900	0.31 (27)	2.0 (9)	0.72 (18)	0.27 (30)	2.3 (32)	0.14 (31)
1000	0.41 (28)	1.8 (7)	0.72 (27)	<0.1	1.8 (39)	<0.07
mCi/km ² to						
1000 m	0.22	1.4	0.54	0.22	2.4	0.39

^aValues in parentheses are the 1 σ counting error expressed as percent of the listed value.

$$\text{The } \overline{K_d} \text{ of } ^{239+240}\text{Pu} : ^{241}\text{Am} \text{ to } 1000 \text{ m} = \text{mCi/km}^2 \frac{^{239+240}\text{Pu} \text{ prefilter/solution}}{^{241}\text{Am} \text{ prefilter/solution}} = 0.06$$

Table 11. Transuranics in the Water Column to 1000m at Station JAO
16°39'31"N 169°24'27"W-6/81.

Depth (m)	239+240Pu ^a (fCi/liter)		241Am (fCi/liter)		241Am:239+240Pu	
	Prefilter	Solution	Prefilter ^b	Solution	Prefilter	Solution
Surf	<0.1	0.13 (37)		<0.03		<0.2
100	0.02 (50)	<0.1		0.11 (50)		--
200	<0.01	0.19 (26)		0.07 (20)		0.34 (33)
300	<0.1	1.15 (8)		0.29 (25)		0.26 (26)
400	0.06 (45)	1.09 (9)		0.07 (60)		0.06 (60)
500	0.15 (23)	1.04 (12)		0.20 (37)		0.19 (39)
600	0.06 (60)	1.17 (11)		0.24 (30)		0.20 (30)
700	0.33 (25)	0.92 (9)		0.36 (47)		0.39 (48)
800	0.15 (28)	1.1 (35)		<0.2		<0.2
900	0.25 (27)	0.71 (14)		0.17 (30)		0.24 (33)
1000	0.24 (27)	0.81 (2)		0.21 (30)		0.24 (32)
mCi/km ² to						
1000 m	0.13	0.79	--	0.18		0.23

^a Values in parentheses are the 1 σ counting error expressed as the percent of the listed value.

^b Analysis incomplete.

upper 1000 m at WBO originate from Bikini and are supplemented by global fallout concentrations typical for this region.

where $^{239+240}\text{Pu}$ concentrations in solution from all depths sampled at WBO exceed that for particulate materials filtered, the opposite is true for ^{241}Am . The concentration ratios show different but substantial enrichment of ^{241}Am over $^{239+240}\text{Pu}$ on the particulate fraction throughout the water column. At stations WBO and JAO, 14% of the total plutonium inventory in the water column to a depth of 1000 m is associated with particulates whereas 71% of the total ^{241}Am inventory at WBO is bound to particles. This partitioning between ^{241}Am and $^{239+240}\text{Pu}$ in the ocean is not a feature related to the source term for the radionuclides.

Pentreath et al. (1980) find the K_d values of ^{241}Am , determined for particulate material in surface seawater within and outside the Irish Sea, are from 2.5 to 7.8 times greater than the respective values for $^{239+240}\text{Pu}$. Beasley and Cross (1980) show results from the Mediterranean where an average of 10% of fallout ^{241}Am is retained on filters compared to only 3.8% of the total $^{239+240}\text{Pu}$.

Extraction experimental results from our laboratory, using different sediments from Enewetak also show that ^{241}Am is more strongly associated with lagoon sediments than $^{239+240}\text{Pu}$ (Table 12). The K_d values for ^{241}Am are 3.3 to 18 times greater than those for $^{239+240}\text{Pu}$ for the set of samples tested. All this suggests there would be a lesser, if any, tendency for ^{241}Am to be mobilized from either sedimentary or particulate material as a dissolved species to solution.

Table 12. Comparative K_d Values for $^{239+240}\text{Pu}$ and ^{241}Am .^a

ID	$^{239+240}\text{Pu}$			^{241}Am		
	Solution MSD # (fCi/liter)	Solid pCi/g	^b K_d $^{239+240}\text{Pu}$	Solution (fCi/liter)	Solid pCi/g	K_d ^{241}Am
224	56 ± 2	27.3 ± 0.5	4.8×10^5	6.7 ± 2.6	28.6 ± 1.9	4.3×10^6
226	41 ± 2	21.3 ± 0.2	5.2×10^5	3.1 ± 2.9	16.9 ± 0.8	5.4×10^6
228	109 ± 3	35.5 ± 0.3	3.3×10^5	3.0 ± 1.8	14.1 ± 0.7	4.7×10^6
230	83 ± 2	32.7 ± 0.3	3.9×10^5	7.6 ± 3.3	9.3 ± 1.0	1.3×10^6
236	173 ± 3	19.8 ± 0.2	1.1×10^5	2.2 ± 1.9	4.3 ± 0.6	2.0×10^6
MEAN			$3.7 \pm 1.6 \times 10^5$			$3.5 \pm 1.8 \times 10^6$

^aDetermined from grab samples of sediment and seawater transferred to containers and mixed during a 2 mo storage period; mixed-size range of solids. Seawater filtered through 0.45-μm filter prior to analysis.

^b K_d pCi • kg⁻¹ dry wt solid/pCi • kg⁻¹ water.

Table 13 shows a selected number of results from Enewetak and Bikini comparing the $^{239+240}\text{Pu}:$ ^{241}Am concentrations in solution and in association with particulate material. Although the levels of ^{241}Am in solution within the lagoons are small they are, nevertheless, an order of magnitude greater than the fallout levels in the surface waters of the north equatorial Pacific. All results have been corrected for any ^{241}Am ingrowth from ^{241}Pu decay between the time of collection and separation. Small but measurable amounts of ^{241}Am are also capable of mobilizing from sedimentary deposits to solution.

The mean activity ratio of $^{241}\text{Am}:$ $^{239+240}\text{Pu}$ associated with the particulate material is essentially identical to the mean sediment inventory ratio at each atoll (see section 2.1). There is a large reduction in this ratio for the radionuclides in solution compared to the values associated with the particulates and, by analogy, the sediments. The ^{241}Am is more strongly bound to the solid phases and is therefore less likely to desorb into solution than plutonium.

In the final column of Table 13, ratios of $^{239+240}\text{Pu}:$ ^{241}Am concentrations are shown, which relate to the ratio of the K_d for the two transuranics. The mean K_d ratio of 0.13 agrees well with the average ratio of 0.11 for values shown in Table 12, determined in the laboratory experiments. The value of the mean ratio determined from the inventories in the water column at WBO, shown in Table 10, is 0.06. This is roughly half the value for the ratio determined in the lagoons and suggests that a larger fraction of the total

Table 13. The $^{239+240}\text{Pu}$ and ^{241}Am Concentrations in Lagoon Seawater and Particulates.

Location	Date	$^{239+240}\text{Pu}$ (fCi/liter)		^{241}Am (fCi/liter)		K_d ($^{239+240}\text{Pu}$: ^{241}Am) ^a	
	Sampled	Prefilter	Solution	Prefilter	Solution	Prefilter	Solution
Enewetak							
Mid Lagoon	8/74	--	30 (5) ^b	--	1.8 (39)	--	0.06 (39)
Mid Lagoon	4/79	4.4 (5)	--	0.96 (13)	--	0.24 (13)	--
Mid Lagoon	4/79	3.5 (5)	--	0.75 (12)	--	0.21 (13)	--
Mid Lagoon	10/79	3.2 (5)	--	1.47 (6)	--	0.46 (8)	--
Mid-Lagoon	10/79	5.2 (3)	--	1.62 (4)	--	0.31 (5)	--
E-24 Lagoon	10/79	20.2 (2)	22.6 (2)	3.3 (7)	1.1 (26)	0.16 (7)	0.05 (26)
E-24 Reef	10/79	76 (2)	58 (3)	8.7 (9)	1.1 (25)	0.11 (9)	0.02 (25)
E-10 Reef	10/79	242 (3)	4.4 (5)	151 (3)	0.46 (30)	0.62 (4)	0.10 (30)
E-24 Reef	10/79	26.4 (1)	63 (2)	13.4 (5)	1.7 (17)	0.51 (5)	0.027 (17)
E-24 Reef	11/80	--	37 (3)	--	0.66 (35)	--	0.018 (35)
E-24 Reef	1/81	--	44 (2)	--	0.42 (38)	--	0.008 (38)
E-24 Reef	7/81	--	29 (2)	--	0.66 (20)	--	0.023 (20)
MEAN	--	--	--	--	--	0.33 (55)	0.038 (79)
Bikini							
B-10	11/78	3.0 (9)	7.6 (4)	2.36 (8)	0.48 (50)	0.78 (9)	0.063 (50)
B-2	11/78	53.9 (5)	48.0 (2)	42.6 (5)	3.3 (30)	0.79 (7)	0.068 (30)
B-6	11/78	98 (4)	23.0 (3)	88 (4)	0.6 (65)	0.90 (6)	0.026 (65)
B-13	11/78	6.9 (7)	39.1 (2)	5.71 (6)	1.15 (45)	0.82 (9)	0.029 (45)
MEAN	--	--	--	--	--	0.82 (7)	0.046 (48)
MEAN	--	--	--	--	--	--	--
Equatorial	--	--	--	--	--	--	0.13
Pacific Surf	--	--	--	--	--	--	--
Water (18) ^c	6-11/78	0.04 (44)	0.28 (44)	0.06 (51)	0.13 (75)	--	--

^a K_d ratio = (fCi/liter) particulate/(fCi/liter) solution.

^bThe 1 σ counting error expressed as percent of the listed value.

^cNumber of samples averaged.

dissolved plutonium found in the water column outside the lagoons is in the oxidized state compared to the average 78% for oxidized forms in solution within the lagoons.

3.6 Residence Time of $^{239+240}\text{Pu}$ and ^{241}Am in the Lagoons

Results interpreted from biological indicators and from direct measurements shown here of the mean water concentrations at Enewetak (for example), indicate the average amount of $^{239+240}\text{Pu}$ in solution at any time has been constant since at least 1965 or for the past 18 y. Mobilized plutonium has originated from a sufficiently large reservoir so that the amount lost to solution over the years has not substantially depleted the sedimentary inventory. A fraction of the $^{239+240}\text{Pu}$ and ^{241}Am in the water (see Tables 3 and 13) is associated with particulates, some of which are resuspended from the bottom sediments. Very little sedimentary material escapes from the lagoon and resuspended bottom material probably settles out on the lagoon floor. Therefore no $^{239+240}\text{Pu}$ or ^{241}Am associated with particulates is assumed lost from the lagoon.

Physical circulation data accumulated recently at Enewetak by Atkinson et al. (1981) indicate that the mean exchange rate for the lagoon water mass with the ocean is approximately 1 mo. The authors point out, however, that water entering the northern portion of the atoll, where sediments have the highest concentrations of plutonium, takes about 4 mo to exit the lagoon. Von Arx (1948) estimates that 7 volumes of Bikini Lagoon water exchange annually with the ocean.

These rates are substantially faster than the mean exchange rate of 140 d estimated for $^{239+240}\text{Pu}$ from radiological data associated with several biological indicators. Using this latter value as the rate at which the $^{239+240}\text{Pu}$ in solution is exchanged between the lagoon and the open ocean, we previously arrived at a mean life for the plutonium in the sedimentary reservoir at Enewetak (to a depth of 16 cm) as 435 y (half residence time is 330 y) (Noshkin and Wong, 1980).

Equation 1 was used to compute this value where dn/dt is the annual rate of curies of plutonium lost from the lagoon and N is the total sedimentary inventory (curies) from which the mobilized $^{239+240}\text{Pu}$ is derived (Noshkin and Wong, 1980).

The half residence time is equal to $\ln 2 \times t$.

$$\bar{t} = \frac{N}{dn/dt} \quad (1)$$

Loss of $^{239+240}\text{Pu}$ by radiological decay was neglected in the above and in subsequent calculations. At Bikini, the computed mean life for $^{239+240}\text{Pu}$ in the sediments, to a depth of 16 cm in the sediment column, was 460 y.

The average $^{241}\text{Am} : ^{239+240}\text{Pu}$ concentration ratios in solution from Table 13 are 0.038 and 0.046 at Enewetak and Bikini, respectively. Multiplying these values by the $^{239+240}\text{Pu}$ mean inventories in solution provides mean curies of 0.036 and 0.06 as the dissolved quantities of ^{241}Am in solution at Enewetak and Bikini Atolls. Using the water residence time of 140 d, 0.09 and 0.16 Ci of ^{241}Am are lost annually from Enewetak and Bikini. Assuming again

that the inventory to a depth of 16 cm in the sediment column is the reservoir for the mobilized ^{241}Am , the mean life, neglecting radioactive decay, exceeds 4000 y. Since the radiological mean life of ^{241}Am is 625 y ($t_{1/2}=433$ y), the effective mean lifetime for ^{241}Am in the sedimentary reservoir is 555 y. With the exchange rates and inventory values used, ^{241}Am will be depleted in the sedimentary reservoirs at the atolls primarily by radioactive decay while $^{239+240}\text{Pu}$ will be lost by mobilization and exchange with the open ocean. This assumes that the mobilization process continues at the same rate in subsequent years.

The previous assessments were made using an exchange rate of 140 d and a sedimentary reservoir extending from the sediment-water interface to a depth of 16 cm. The depletion rate of plutonium and americium from the lagoons clearly depends on the water exchange rate between the lagoon and ocean the size and depth of the reservoir from which the mobilized $^{239+240}\text{Pu}$ or ^{241}Am is derived. The evidence provided by Von Arx (1948) and Atkinson et al. (1981), indicating that the exchange rate of water and its dissolved constituents between the lagoon and ocean is more rapid than 140 d, cannot be dismissed. There is some evidence that plutonium contained in subsurface sediments is lost to the overlying water by vertical movement of the interstitial water. However, we do not know the active depth in the sediment column through which plutonium can move as a result of advection or diffusion along concentration gradients. In addition, we have not assessed the importance of this mechanism relative to other physical,

biological, or chemical disturbances that may result in resuspension of sediment to the water column followed by plutonium mobilization to solution.

If it is assumed that the water and its dissolved constituents exchange between Enewetak Lagoon and the ocean every 30 d, for example, and the principal reservoir for plutonium is only the surface 2.5-cm sediment layer, then the mean and half residence times for $^{239+240}\text{Pu}$ in this reservoir are only 21 and 15 y, respectively. The mean and half life for ^{241}Am computed for these conditions are 416 and 289 y, respectively.

This computation shows that the mean quantity of plutonium mobilized to solution during 1982 should be half the average amount it was 15 y ago. The ^{241}Am levels would remain essentially unchanged during this period.

Our measurements do not support this rapid a rate of plutonium disappearance from the lagoon. Either the residence time for the lagoon water is substantially longer than 30 d or the size of the active sedimentary reservoir extends deeper than 2.5-cm. Using an exchange rate of 1 mo at Enewetak and the quantity of plutonium contained in the reservoir to a depth of 16 cm as N, the mean and half residence times of $^{239+240}\text{Pu}$ are 103 and 71 y, respectively. The mean and half life for ^{241}Am are, respectively, 400 and 277 y. For this example, our present measurements of mean lagoon concentrations lacks the degree of precision necessary to distinguish if this rate is reasonable.

Work to resolve the correct rates of plutonium and americium loss from both lagoons is currently a high priority program. The rate of plutonium disappearance from the sediments could be much more rapid than previously estimated.

4. CONCLUSION

Little reliable information is available to predict the fate of transuranics in the deep sea. Only from the accumulation and comparison of results from different sources in the environment can a clearer understanding of the behavior of transuranics in the ocean be developed and universal characteristics identified. The work described herein is relative to this objective.

Strong association of both $^{239+240}\text{Pu}$ and ^{241}Am is found with the sediments, but we find that $^{239+230}\text{Pu}$ is less firmly bound and is capable of more rapid mobilization from the sediments at Bikini and Enewetak Atolls. Small amounts of ^{241}Am are also capable of dissociating from marine sediments. The partitioning of ^{241}Am between sediments and water is controlled by the law of mass action, and the mechanism can be considered reversible. The amount of $^{239+240}\text{Pu}$ mobilized to solution at the atolls can be reasonably predicted using a K_d of approximately 2.3×10^5 and the mean sediment concentrations. This value also provides reasonable estimates of the quantities mobilized to solution at Rongelap Atoll, Johnston Atoll, and from sedimentary deposits at San Clemente Island, California.

The mobilized $^{239+240}\text{Pu}$ at Enewetak and Bikini has solute-like characteristics and different valence states coexist in solution. The largest fraction of the soluble plutonium is in an oxidized form (+V or VI). Quantities associated with suspended particulate material and sediments are predominately in the reduced state (+III or IV). The sorption-desorption process is not completely reversible because of changes that occur in the relative amounts of the mixed oxidation states in solution with time. The oxidized forms of $^{239+240}\text{Pu}$ in solution have a lesser tendency to associate with sedimentary or particulate material than reduced plutonium. Complexation after mobilization also affects the resorption rate. Therefore, any characteristics of $^{239+240}\text{Pu}$ described at a point of reference may not necessarily be relevant to explain behavior after mobilization and migration in solution.

Water profiles to 1000-m depth in the equatorial Pacific show that ^{241}Am $^{239+240}\text{Pu}$ ratios are more than a factor of two higher in the particulate phase than in the soluble phase. This separation is mediated by the higher solubility of plutonium relative to americium. Since ^{241}Am and $^{239+240}\text{Pu}$ associated with particulates should move vertically in the water column more rapidly than the species in solution, the rate of vertical transport of ^{241}Am to deep bottom sediments can be assumed more rapid than $^{239+240}\text{Pu}$. As the lagoon studies show, once in the sediment, ^{241}Am will be remobilized to solution at a slower rate than $^{239+240}\text{Pu}$. Some fraction of $^{239+240}\text{Pu}$ placed on the surface of the sea floor should, in time, disperse in the overlying water mass and migrate from its original

site. The ^{241}Am should remain more firmly fixed to the sedimentary material near the point of introduction. The rate of disappearance of the two radionuclides will depend on the physical, biological, and chemical characteristics of the sedimentary deposits and the rate of water movement into and out of the contaminated region. The relative amounts of ^{241}Am to $^{239+240}\text{Pu}$ in the sedimentary deposits at Enewetak and Bikini will be altered in future years as a result of plutonium mobilization and the radiological decay of ^{241}Am .

It is not now possible, with the results available, to make longterm predictions of the relative quantities remaining in the atolls' sediments. These predictions rely on accurately knowing the size of the sedimentary reservoir capable of continuously supply plutonium to the overlying water and the mean residence time for the dissolved plutonium in the lagoon water mass. These parameters are not well known.

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REFERENCES

- Atkinson, M., S. V. Smith, and E. D. Stroup. 1981. Circulation in Enewetak Atoll Lagoon. Limnology and Oceanography, 26, 1074-1083.
- Beasley, T. M. and F. A. Cross. 1980. A review of biokinetic and biological transport of transuranic radionuclides in the marine environment. In: Transuranic Elements in the Environment, w C. Hanson (Ed.) DOE/TIC-22 800, U.S. Department of Energy, Washington, District of Columbia, pp. 524-540.
- Bojanowski, R., H. D. Livingston, D. L. Schneider and D. R. Mann. 1975. A procedure for analysis of americium in marine environmental samples. In: Reference Methods of Marine Radioactivity Studies II, Technical Reports Series. No. 169. International Atomic Energy Agency, Vienna. pp 77-86.
- Carpenter, R. and T. M. Beasley. 1981. Plutonium and americium in anoxic marine sediments: evidence against mobilization. Geochimica et Cosmochimica Acta, 45, 1917-1930.
- Edgington, D. N. 1981. A review of the persistence of long-lived radionuclides in the marine environment--sediment/water interactions. In: Impacts of Radionuclide Releases into the Marine Environment. Proceedings of Symposium, Vienna, 6-10 Oct., 1980. International Atomic Energy Agency, Vienna, pp 67-91.
- Lovett, M. B. and D. M. Nelson. 1981. Determination of some oxidation states of plutonium in seawater and associated particulate matter. In: Techniques for Identifying Transuranic Speciation in Aquatic Environments. Proceedings of Meeting Ispra, 24-28 Mar., 1980. International Atomic Energy Agency, Vienna, pp 27-35.

- Nelson, D. M. and M. B. Lovett. 1981. Measurements of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea. In: Impacts of Radionuclide Releases into the Marine Environment. Proceedings of Symposium, Vienna, 6-10 Oct., 1980. International Atomic Energy Agency, Vienna, pp 105-118.
- Nelson, D.M. and D.N. Metta. 1983. The Flux of Plutonium from Sediments to Water in Lake Michigan in Radiological and Environmental Research Division Annual Report. Argonne National Laboratory, ANL-8R-65, Part 3. pp31-36.
- Noshkin, V. E. 1980. Transuranium radionuclides in components of the benthic environment of Enewetak Atoll. In: Transuranic Elements in the Environment, W.C. Hanson (Ed.) DOE/TIC-22800, U.S. Department of Energy, Washington, District of Columbia, pp. 578-601.
- Noshkin, V. E., J. L. Brunk, T. A. Jokela, and K. M. Wong. 1981. ²³⁸Pu Concentrations in the Marine Environment at San Clemente Island. Health Physics, 40, 643-659.
- Noshkin, V. E., R. J. Eagle, K. M. Wong, and T. A. Jokela. 1981. Transuranic concentrations in reef and pelagic fish from the Marshall Islands. In: Impacts of Radionuclide Releases into the Marine Environment. Proceedings of Symposium, Vienna, Oct. 1980. International Atomic Energy Agency, Vienna, pp 293-317.
- Noshkin, V. E. and K. M. Wong. 1980. Plutonium mobilization from sedimentary sources to solution in the marine environment. In: Marine Radioecology. Proceedings of 3rd Nuclear Agency Seminar, Tokyo, 1-5 Oct. 1979, Nuclear Energy Agency/OECD, Paris, pp. 165-178.

Noshkin, V. E., K. M. Wong, R. J. Eagle and C. Gatrouris. 1974.

Transuranics at Pacific Atolls, 1. Concentrations in the waters at Enewetak and Bikini, UCRL-51612, Lawrence Livermore National Laboratory, Livermore, California, 30 pp.

Noshkin, V. E., K. M. Wong, T. A. Jokela, R. J. Eagle and J. L. Brunk. 1978. Radionuclides in the Marine Environment Near the Farallon Islands. UCRL-52381, Lawrence Livermore National Laboratory, Livermore, California, 17 pp.

Pentreath, R. J., D. F. Jefferies, M. B. Lovett, and D. M. Nelson. 1980. The behaviour of transuranic and other long-lived radionuclides in the Irish Sea and its relevance to the deep sea disposal of radioactive wastes. In: Marine Radioecology. Proceedings of 3rd Nuclear Energy Agency Seminar, Tokyo, 1-5 Oct., 1979. Nuclear Energy Agency/OECD, Paris, pp 203-221.

Schell, W. R., F. G. Lowman, and E. P. Marshall. 1980. Geochemistry of transuranic elements at Bikini Atoll. In: Transuranic Elements in the Environment, W.C. Hanson (Ed.). DOE/TIC-22800, U.S. Department of Energy, Washington, District of Columbia, pp. 541-577.

Von Arx, W. W. 1948. The Circulation Systems of Bikini and Rongelap Lagoons. Transactions American Geophysical Union, 29, 861-870.

Wong, K.M. 1971. Radiochemical Determinations of Plutonium in Seawater, Sediments and Marine Organisms, Analytica Chimica Acta 56, 355-364.

Wong, K. M., G. Brown, and V. Noshkin. 1978. A Rapid Procedure for Pu Separation in Large Volumes of Fresh and Saline Water by Manganese Dioxide Coprecipitation. Journal of Radioanalytical Chemistry, 42, 7-15.

Wong, K. M., J. L. Brunk, and T. A. Jokela. 1983. Radiochemical Procedures Used in the Environmental Sciences Division, LLNL, for the Analysis of Selected Radionuclides in the Marine Environment. In press, Lawrence Livermore National Laboratory Livermore, California.

Wong, K. M., T. A. Jokela, and V. E. Noshkin. 1980. Problems associated with transuranium determination of suspended solids in sea water samples. In: Radioelement Analysis Progress and Problems, W. S. Lyon (Ed.). Ann Arbor Press, Ann Arbor, pp. 207-214.

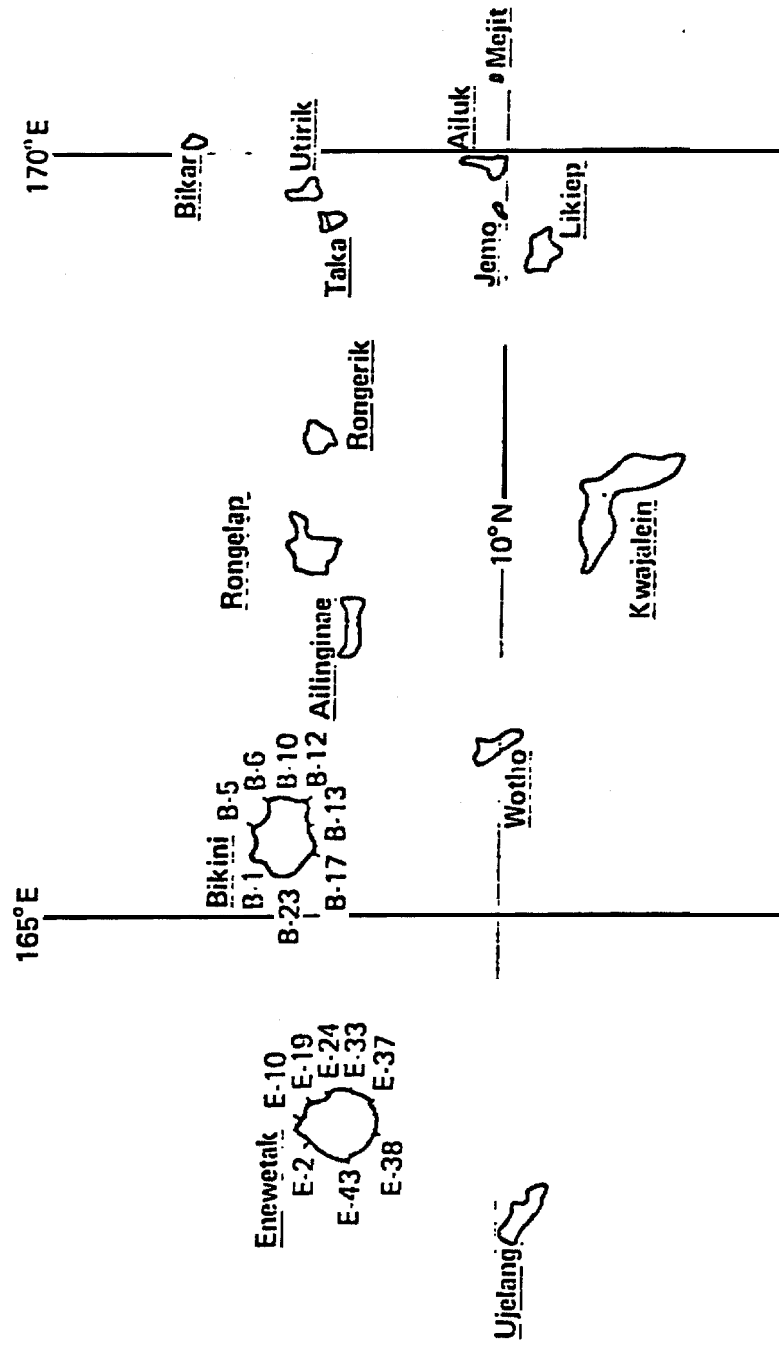


Fig. 1. Geographic locations of Enewetak, Bikini, and other Marshall Islands Atolls.

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